Experimental report

18/10/2018

Proposal: DIR-167 **Council:** 4/2018

Title: Crystal structure of UPt2Si2 at elevated temperatures

Research area:

This proposal is a new proposal

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Experimental team: Karel PROKES

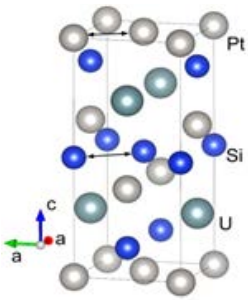
Local contacts: Oscar Ramon FABELO ROSA

Samples: UPt2Si2

Instrument	Requested days	Allocated days	From	To
D9	3	3	12/10/2018	15/10/2018

Abstract:

Uranium based intermetallic compounds have been in a focus of an intensive research for many years due to their unique physical properties of unfilled 5f electron wave functions. Their vicinity to the Fermi level and participation in bonding properties due to their large spatial extent leads to a large number of crystallographic modifications. Most of tetragonal UT_2X_2 compounds (*T* stands for a late a transition metal and *X* for Si or Ge) comprising more than 20 members adopt the $ThCr_2Si_2$ type of structure (space group *I4 m m m*). However, few of them, namely those with *T* = Ir or Pt are reported to crystallize in the primitive tetragonal $CaBe_2Ge_2$ type of structure (space group *P4/ n m m*). Common for both these structures is the absence of *(h 0 0): h = 2n + 1* and *(h k 0): h + k = 2n + 1* reflections that are systematically extinct due to an n-type glide plane. The subject of the performed study was the determination of the crystal structure of UPt_2Si_2 that is reported to adopt the latter, primitive version (see Fig. 1) [1-3]. Previously, a great attention has been paid to a possible crystallographic disorder [4] that has been linked to irreversibility of magnetic behavior [5]. Previous neutron powder and single crystal diffraction experiments have indicated that one of the two Pt and two Si atomic positions exhibit anomalously large displacement parameters [4]. However, recently we have observed, using a large UPt_2Si_2 single crystal glued to a sample holder that also Bragg reflections violating the extinction rules exist. The typical intensity ratio between these forbidden and allowed reflections was 1 : 1000, i.e. much larger than possible contamination due to λ/2 contamination.



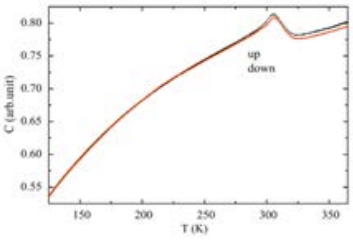


Fig. 1 (left): Schematic representation of the tetragonal $CaBe_2Ge_2$ type of structure (space group *P4/ n m m*). Sites that were expected to be non-equivalent are linked by arrows.

Fig. 2 (right): Specific heat of the as-cast UPt_2Si_2 (according to [4]).

We were speculating that the space group given in the literature is in error and that the glide plane connecting two of the Pt (and two Si) (in Fig. 1 linked by arrows) atoms is missing. Different models were proposed, among them a different degree of occupation, mixing of atoms, different thermal factors at the two sites and a subtle orthorhombic distortion have been considered. All these mechanisms would lead to an existence of *(h 0 0): h = 2n + 1* and *(h k 0): h + k = 2n + 1* reflections.

The situation in the case of UPt_2Si_2 is however complicated due to a confirmed structural transition occuring around room temperature (Fig. 2) below which another crystal structure exists, leading to yet another possible scenario that the observed forbidden reflections are due to strain in the sample caused by the stiff glue. To be able to distinguish between different scenaria we have undertaken a diffraction experiment on relatively fresh small single

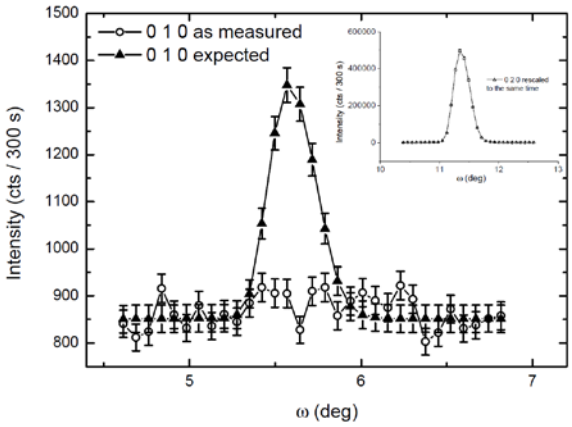


Fig. 3: Rocking curve through the 0 1 0 reciprocal position recorded with measurement time of 300 sec per point (open symbols) together with re-scaled intensity of the 0 2 0 Bragg reflection divided by a factor of 1000 (closed symbols). In the inset, the measured 0 2 0 rocking curve rescaled for the same time is shown.

crystal that was not cycled through the structural transition many times.
The experiment was carried out on the D9 hot neutron diffractometer operated in the four-circle mode. For the experiment the 21 mg heavy crystal with size of approximately 1x1x2 mm^3 has been wrapped in an aluminium foil that has been fixed on the sample holder pin using dedicated high-temperature glue. In this way we have minimalized the stress acting on the sample. Data were collected mostly well above the transition temperature, at 400 K, achieved using a four-circle furnace. In total, we have recorded, before the reactor went unexpectedly down, 457 Bragg reflections, 292 unique. Among those were also 22 Bragg reflections that are forbidden for the space group *P 4/n m m*. Allowed reflections were recorded with time 5 sec per point, forbidden ones mostly with 128 sec per point, in part with 300 sec per point. In few cases a small intensity has been detected at the forbidden reflection positions. This, however, has been proved to be due to small residual λ/2 contamination. In Fig 3 we show the curve through the 0 1 0 reciprocal position recorded with measurement time of 300 sec per point utilizing an additional Er filter together with signal that would be expected if the same ratio of 1 : 1000 would be preserved as in the case of measurement on a large crystal at HZB. In the inset of Fig. 3 we show, the measured 0 2 0 rocking curve rescaled for the same time as used for measurement at the 0 1 0 position. Clearly, no intensity is detected at the 0 1 0 position and the expected signal is not present. It seems therefore quite clear that the n-glide mirror plane is present and that the crystal structure of UPt_2Si_2 is of the $CaBe_2Ge_2$ type. The space group is *P 4/n m m* and the forbidden reflections seen in our former experiments are due to internal stress within the big glued single crystal. This insight is very important for us.

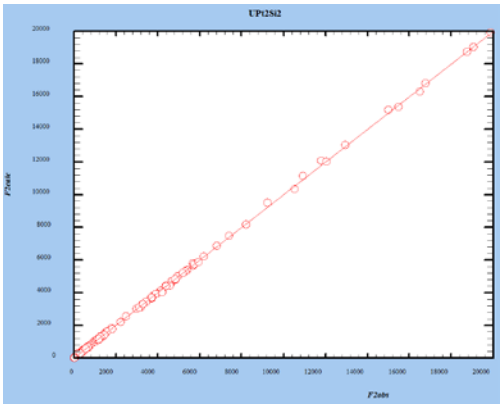


Fig. 4: Calculated versus observed structure factors squared recorded on UPt_2Si_2 at 400 K using D9.

The recorded data were used in the refinement of the crystallographic details, in particular the positional and the temperature displacement parameters. These findings are in agreement with previous studies [3]. The agreement is excellent (Fig. 4), leading R_F = 2.78 if only isotropic temperature factors and R_F = 1.88 if anisotropic temperature factors are considered. The positional parameters were refined to be x_U = 0.74833 (4), x_{Pt} = 0.37868 (4) and x_{Si} = 0.13357 (4). All these atoms are in the 2c (¼ ¼ z) position. We have also identified enhancement of the temperature displacement factors for Pt atoms at the 2a and Si atoms at the 2c positions. These are, however, somewhat smaller than in the literature [3].

In conclusion, the performed experiment showed that the high temperature crystal structure of UPt_2Si_2 is of the $CaBe_2Ge_2$ type. We have gained important insights regarding the relation of this high-temperature crystal structure to the low-temperature distortion. We would like to thank ILL for providing us with the experimental beam time within the director's discretionary time scheme and O. Fabelo for his support during and after the experiment.

References

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